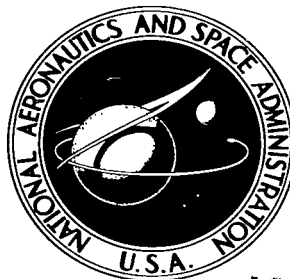


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# MASS SPECTROMETRIC INVESTIGATION OF REACTIONS OF OXYGEN ATOMS WITH HYDROGEN AND AMMONIA

*by Edgar L. Wong and Andrew E. Potter, Jr.*

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*Cleveland, Ohio*



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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

The reactions of atomic oxygen with hydrogen and with ammonia were studied in the near-absence of molecular oxygen. A stirred reactor was used to make reaction rate measurements, and the gases from the stirred reactor were analyzed with a Bendix time-of-flight mass spectrometer. Quantitative analyses of atomic oxygen as well as several of the reaction products were performed with this instrument.

The reaction rate of the hydrogen - atomic oxygen ( $\text{H}_2 + \text{O}$ ) reaction was investigated in the temperature range  $400^\circ$  to  $600^\circ$  K. Analysis showed that the only detectable products of the reaction were molecular oxygen, water, and atomic hydrogen ( $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{H}$ ). With this information, a mechanism for the reaction was written. The mechanism and the experimental data were used to find the rate constant for the  $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$  reaction. The result was  $4.3 \times 10^{13} \exp(-10.2/RT)$  cubic centimeter per mole per second (where  $R$  is the universal gas constant and  $T$  is the absolute temperature), which is in good agreement with rate constants found by other investigators. In a previous work by the authors the rate of  $\text{O}$  disappearance by reaction with  $\text{H}_2$  in the presence of a large excess of  $\text{O}_2$  was measured. Under these circumstances, the rate was about four times larger than that for the reaction in the absence of  $\text{O}_2$ . This result was explained quantitatively by the reaction sequence  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ ;  $\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$ .

The reaction rate of the ammonia - atomic oxygen ( $\text{NH}_3 + \text{O}$ ) reaction was investigated in the temperature range  $350^\circ$  to  $600^\circ$  K. Product analyses indicated that the stoichiometry of the reaction could be represented by  $\text{NH}_3 + 4.4 \text{ O} \rightarrow \text{NO} + 0.5 \text{ H}_2 + 1.2 \text{ O}_2 + 1.0 \text{ H}_2\text{O}$ . The rate of the reaction was unaffected by the presence or absence of  $\text{O}_2$ , so that the previous rate constant for  $\text{O}$  disappearance of  $3 \times 10^{12} \exp(-4.8/RT)$  cubic centimeter per mole per second is unchanged. A mechanism that explains the lack of effect of  $\text{O}_2$  was suggested for the oxidation reaction. From this mechanism and the reaction stoichiometry it was deduced that the rate of the reaction  $\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH}$  was about one-fourth the rate of  $\text{O}$  disappearance, or  $1 \times 10^{12} \exp(-4.8/RT)$  cubic centimeter per mole per second.

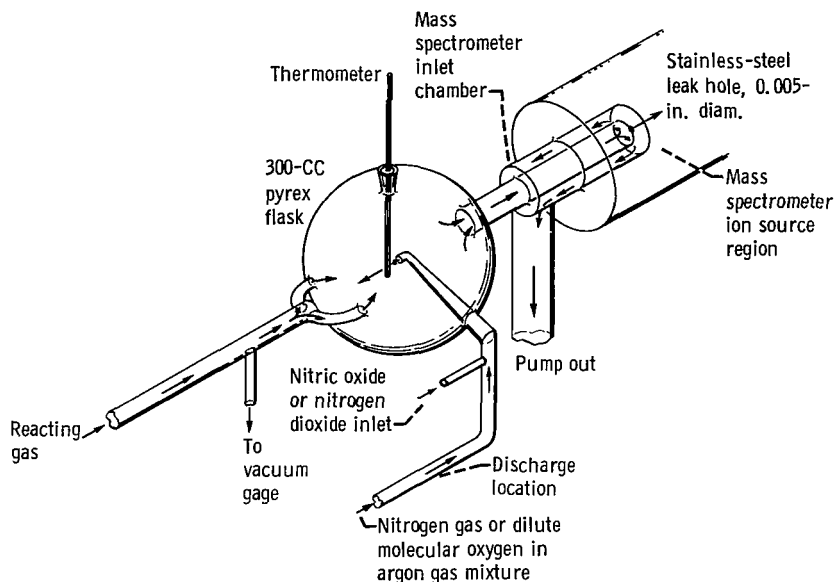


Figure 1. - Stirred reactor and connection to mass spectrometer.

## INTRODUCTION

The study of elementary reactions involving atomic oxygen ( $O$ ) is important, because these reactions are common in situations of practical or scientific interest, as in flames of jet or rocket engines or in the upper atmosphere. In a previous work by the authors (ref. 1) the rates of reaction of  $O$  with hydrogen ( $H_2$ ), ammonia ( $NH_3$ ), and methane ( $CH_4$ ) in the presence of a large excess of molecular oxygen ( $O_2$ ) were measured. Since it seemed likely that  $O_2$  entered the reaction by combining with some of the reaction intermediates, the reaction rate measurements for  $H_2$  and  $NH_3$  were repeated, this time in the near-absence of  $O_2$ .

For this work, the stirred reactor technique was used again in conjunction with mass spectrometric analysis. Temperatures varied in the range  $400^\circ$  to  $600^\circ$  K, and pressures were about 1 millimeter.

## EXPERIMENTAL

### Apparatus

The 300-cubic centimeter stirred reactor and its connection to the Bendix time-of-flight mass spectrometer (model 14-101) are shown in figure 1 and described in reference 1. One change from the previous arrangement was the use of a stainless-steel leak hole diameter of 0.005 inch instead of the former pyrex leak hole diameter of about 0.01 inch. The smaller metallic leak hole could be used provided that the mass spectrometer sensitivity is at a level high enough to monitor small changes in oxygen atom concentration easily.

## Materials

Gas	Purity, percent
Hydrogen	99.9
Nitrogen	99.9
Oxygen	99.5
Ammonia	99.9
Deuterated ammonia	99.5
Argon	99.9
Nitric oxide	99.5
Nitrogen dioxide	$\geq 99.5$

The various gases used in this work are described in the table at the left. The purity of these gases was checked mass spectrometrically. Nitric oxide was purified by first condensing the gas at liquid-nitrogen temperature and then pumping it. After the removal of noncondensables, the NO gas was raised to  $-140^{\circ}\text{C}$  and passed through a second cold trap at  $-100^{\circ}\text{C}$  to insure the complete removal of nitrogen dioxide ( $\text{NO}_2$ ), which was present in the tanked NO gas. With this treatment, the NO gas was analyzed mass spectrometrically to be at least 99.5 percent pure.

Nitrogen dioxide gas was prepared by adding tanked  $\text{O}_2$  gas to purified NO gas. The mixture was then cooled to  $-70^{\circ}\text{C}$  and evacuated to remove noncondensables. Then the contents were raised to  $-20^{\circ}\text{C}$ , and a portion of the contents was collected in a storage flask to be used in the titration of oxygen atoms.

## Production of Atomic Oxygen

For this investigation it was necessary to produce a stream containing O but with the complete, or nearly complete, absence of  $\text{O}_2$ . This was done in two ways. First, a stream of molecular nitrogen ( $\text{N}_2$ ) was partly (1 to 2 percent) dissociated in a microwave discharge (produced by a Raytheon KVL04 (NB)100-W microwave generator) then NO was added in an amount just sufficient to destroy the nitrogen atoms and replace them with oxygen atoms. This procedure is described in detail in reference 2. The second technique used subjected a stream of argon (Ar) containing 1.8 percent  $\text{O}_2$  to a microwave discharge. The discharge produces about 50 percent dissociation of the  $\text{O}_2$ , and so does not yield a mixture completely free of  $\text{O}_2$  as did the nitric oxide and atomic nitrogen ( $\text{NO} + \text{N}$ ) technique. The concentration of  $\text{O}_2$ , however, is so low that, to a first approximation, it can often be neglected.

## Mass-Spectrometric Monitoring of Oxygen Atom Concentrations

Atomic oxygen can be monitored with the mass spectrometer either at mass-to-charge ratio,  $m/e = 16$  or at  $m/e = 8$ . The former can be used only in the absence of interference from  $\text{O}_2$ ,  $\text{NH}_3$ , or other molecules that yield prominent  $m/e = 16$  peaks. The latter can be used whenever such interference is present. It is definitely preferable to work at  $m/e = 16$  when possible, because the instrument is operated at 30 ionizing electron volts and at a relatively low sensitivity level. In this manner of operation, the noise level is so low that an excellent signal-to-noise ratio can be achieved. When it is necessary to work at  $m/e = 8$ , 85 ionizing electron volts and a very high sensitivity setting is required to monitor O concentration changes. Such operating conditions result in a poor signal-to-noise ratio. The use of  $m/e = 8$  to detect oxygen atoms has been discussed in detail in reference 1.

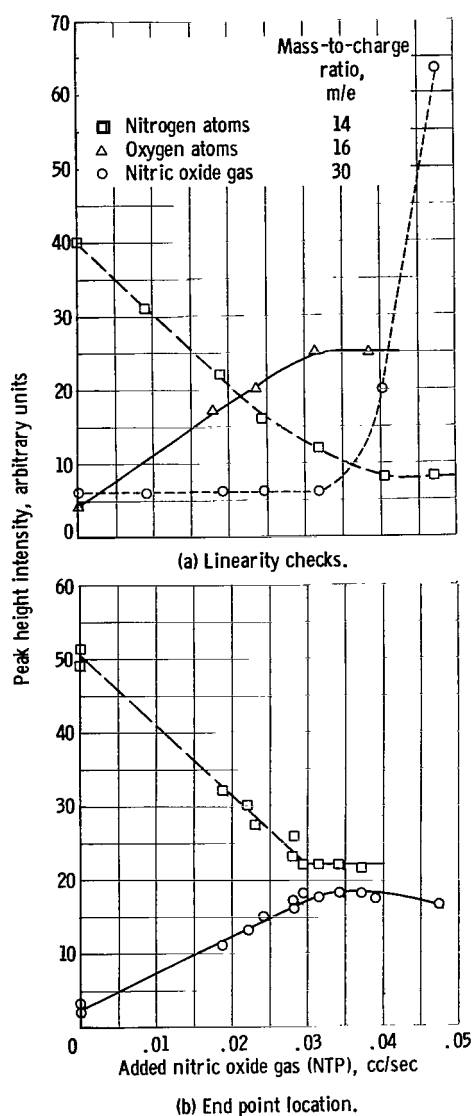


Figure 2. - Titration curves for  $\text{NO} + \text{N} \rightarrow \text{O} + \text{N}_2$  reaction. Bendix operating at 30 ionizing electron volts; nitrogen carrier gas, flow rate, 1.5 cubic centimeters per second (normal temperature and pressure, NTP); system pressure, 0.62 millimeter of mercury.

ence 1 to calibrate the mass spectrometer.

The discharge efficiency of the microwave generator changed slightly with pressure. The experiments were performed over small pressure ranges so that these corrections never exceeded 10 percent (ref. 1). Further discussion of the pressure correction is given in reference 1.

In this report, it was possible to use the peak at  $m/e = 16$  for the reaction of  $\text{H}_2$  with  $\text{O}$ . The  $\text{O}$  was generated by the  $\text{N} + \text{NO}$  reaction so that no  $\text{O}_2$  was present. For the reaction of ammonia with atomic oxygen ( $\text{NH}_3 + \text{O}$ ), however, it was necessary to use the peak at  $m/e = 8$ , because  $\text{NH}_3$  will contribute a strong  $\text{NH}_2$  peak at  $m/e = 16$ .

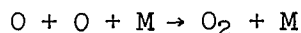
Calibration of the mass spectrometer for  $\text{O}$  was accomplished by causing mixtures containing known concentrations of  $\text{O}$  to flow past the mass spectrometer leak and then relating the ion current at  $m/e = 8$  or 16 to the  $\text{O}$  concentration. Two techniques were used to generate gas streams containing known concentrations of  $\text{O}$ .

In one technique (ref. 2),  $\text{NO}$  was added to a stream of partly dissociated nitrogen until the  $\text{NO}$  flow was just sufficient to react with all the atomic nitrogen ( $\text{N}$ ), thus generating a stream containing only  $\text{N}_2$  and  $\text{O}$ . The flow rate of  $\text{O}$  at this equivalence point is equal to the flow of  $\text{NO}$  into the stream. An illustration of the results of this technique is shown in figure 2, where a typical set of titration curves is shown. The mass spectrometer peak intensity for  $\text{O}$ ,  $\text{N}$ , and  $\text{NO}$  are plotted against the flow rate of  $\text{NO}$  added to the stream of partly dissociated nitrogen. The equivalence point, where the flow of  $\text{NO}$  just equals the flow of  $\text{N}$  before reaction and the flow of  $\text{O}$  after reaction, can be clearly seen in this figure.

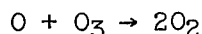
In the second technique,  $\text{Ar-O}_2$  mixtures were dissociated by the microwave discharge, and the  $\text{O}$  concentration was measured by adding  $\text{NO}_2$  until the  $\text{O}$  peak disappeared (ref. 3). The  $\text{NO}_2$  flow rate was then equal to the  $\text{O}$  flow rate. This technique was also used in refer-

### Calculation of Rate Constants

In a previous work (ref. 1) the authors employed mixtures of  $O_2$  and  $O$  containing about 20 percent  $O$ . In this case, it was necessary to correct for the recombination of  $O$  resulting from the reactions



and



where  $M$  is a third body. Now, however, the concentration of  $O$  is about a factor of 10 smaller than before, and the concentration of  $O_2$  is either negligible or is about a factor of 100 smaller than before. As a result, the recombination corrections that were required in the previous work are so small that they can be neglected.

Thus, for the bimolecular reaction of  $O$  with a gas  $B$  in the stirred reactor, the decrease of oxygen atom concentration  $\Delta[O]$  upon the addition of  $B$  is related to the rate constant  $k$  by the following expression

$$\frac{\Delta[O]}{\Delta t} = -k[O][B] \quad (1)$$

where  $\Delta t$  is the residence time of the gases in the stirred reactor and  $[O]$  is the oxygen atom concentration in moles per cubic centimeter in the reactor after the addition of  $B$ . The quantity  $[B]$  is the concentration in moles per cubic centimeter of  $B$  inside the stirred reactor.

The residence time  $\Delta t$  was assumed to be the reactor volume divided by the total volumetric flow rate at the reactor pressure. The concentration of  $O$  before and after addition of the reactant gas  $B$  was measured by the mass spectrometer calibrated as described in the previous section. The concentration of reactant gas  $B$  inside the reactor was obtained by subtracting the amount of  $B$  used up by chemical reaction from the flow rate of  $B$  into the reactor. Dividing this difference by the total flow rate yielded the mole fraction of  $B$ , since the pressure and temperature of the gas in the stirred reactor are known. In the work described in this report only a small fraction of the added gas  $B$  was used up by chemical reaction. Direct measurements of this fraction with the mass spectrometer were subject to the usual instrument noise, so a better procedure was used whereby this fraction was calculated from the amount of  $O$  used in the reaction and the stoichiometry of the reaction. The reaction stoichiometry was calculated from known rate constants for the molecular hydrogen and atomic oxygen ( $H_2 + O$ ) reaction, and was measured from  $NO$  production for the  $NH_3 + O$  reaction, as described in the section Stoichiometry of Reaction, p. 17.

## Precision and Accuracy

For the present work, as in reference 1, the precision of the data herein could be considerably improved by limiting the amount of added gas B to about 15 percent of the total flow. This minimized the pressure correction to the ion current (ref. 1), and especially improved the precision at low temperatures where larger amounts of added gas B were used.

The precision of the mass-spectrometric analyses for reactants and products was poor. Part of the low precision could be attributed to instability of the mass spectrometer. In order to minimize errors due to this instability, all the reaction products were measured simultaneously with the [O] and expressed as ratios to the [O]. Mass-spectrometer calibration curves for each of the reaction products were obtained immediately after a run by adding known amounts of the reaction products to the gas flow. The precision for the measurement of reaction products in terms of ratios to the [O] was about  $\pm 25$  percent for most of the data. Thus, the precision for the analysis of any individual component is about half this value, or about  $\pm 12$  percent.

As discussed in reference 1, this technique leads to a precision of about  $\pm 20$  percent and an accuracy of about  $\pm 50$  percent for the rate constants and an accuracy of about  $\pm 20$  percent ( $\sim \pm 1.5$  kcal) for the activation energies.

## REACTION OF HYDROGEN WITH ATOMIC OXYGEN

The reaction of O and H<sub>2</sub> has been studied by others using a variety of methods (refs. 4 to 7). The object in studying this reaction again was to test the experimental technique used herein and to provide new information on this important reaction.

### Atomic Oxygen Consumption in Stirred Reactor and Order of Reaction

For study of the H<sub>2</sub> + O reaction, O was produced by the N + NO titration technique. A constant flow rate of O into the stirred reactor was maintained by a constant flow of NO into the dissociated nitrogen stream upstream of the reactor. The flow rate of NO was adjusted so that all the nitrogen atoms were replaced by oxygen atoms, with no excess of NO. Then, H<sub>2</sub> was added to the stirred reactor in increasing steps, and the [O] was measured at each step. The results from measurements of this kind at three temperatures are presented in table I and plotted in figure 3. Shown in this figure are plots of  $\Delta[O]/[O]$  against the ratio of the hydrogen flow rate  $F_{H_2}$  to the total flow rate  $F_t$ ,  $F_{H_2}/F_t$ . Since the amount of hydrogen used up by chemical reaction is small,  $F_{H_2}/F_t$  is approximately equal to the mole fraction of hydrogen. Examination of equation (1) for the bimolecular reaction rate expression shows that the plots of  $\Delta[O]/[O]$  against  $F_{H_2}/F_t$  should approximate straight lines at constant pressure. This is shown in figure 3 in which the oxidation reaction closely approximates a bimolecular reaction, first order in both O and H<sub>2</sub>.



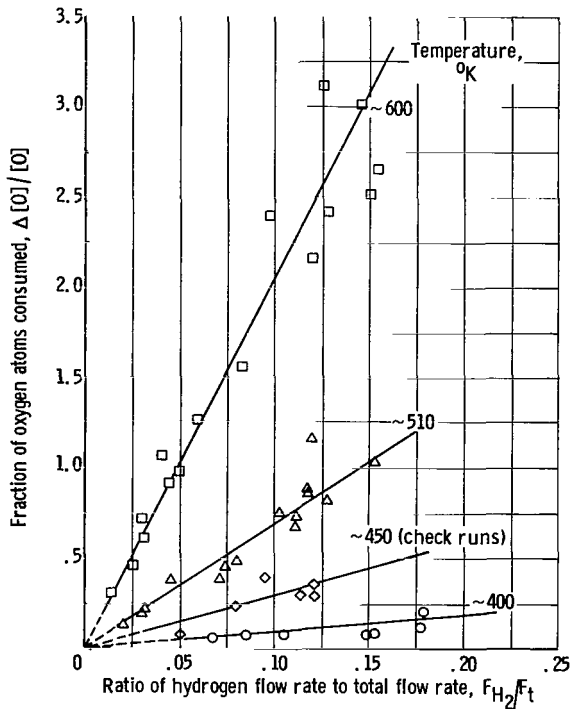


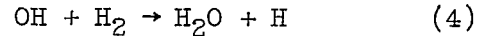
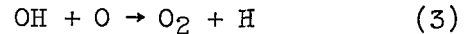
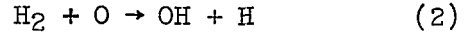
Figure 3. - Oxygen atoms consumed by added molecular hydrogen. Temperature range, 400° to 600° K; nitrogen carrier gas flow rate, 1.5 cubic centimeters per second; system pressure, 0.7 to 0.8 millimeter of mercury.

## Products of Reaction

The only products of the reaction that could be detected were  $O_2$ ,  $H_2O$ , and  $H$ . In reference 1 only  $H_2O$  and  $H$  could be identified as the principal products. The presence of a large excess of  $O_2$  in that case prevented the detection of  $O_2$  as a reaction product.

## Mechanism of Reaction

Enough is known about the reactions of hydrogen with oxygen to allow a mechanism to be written based on the observed products of the reaction and the experimental conditions. This mechanism is



Reaction (4) is selected over the alternate water-forming reaction  $2OH \rightarrow H_2O + O$  because it may be shown (by using rate

constants from ref. 8) that the rate of this reaction must be negligible when compared with reaction (4).

## Calculation of Rate Constant for Reaction $H_2 + O \rightarrow OH + H$

The rate constant  $k_2$  for the initial elementary reaction of  $H_2 + O \rightarrow OH + H$  is of primary interest because it determines to a great extent the overall rate of the oxidation. An expression for  $k_2$  in terms of experimentally measured quantities and the two remaining rate constants  $k_3$  and  $k_4$  can be derived from the reaction scheme of the previous section by assuming the steady state for  $(OH)$ . This expression is as follows (differentials have been replaced by finite differences appropriate to the stirred reactor):

$$\frac{\Delta[O]}{\Delta t} = -k_2[O][H_2] \left[ \frac{2k_3[O] + k_4[H_2]}{k_3[O] + k_4[H_2]} \right] \quad (5)$$

This expression can be rewritten as

$$\frac{\Delta[O]}{\Delta t} = -k_2[O][H_2] \left[ \frac{2 + \frac{k_4 X_{H_2}}{k_3 X_O}}{1 + \frac{k_4 X_{H_2}}{k_3 X_O}} \right] \quad (6)$$

where  $X_{H_2}$  is the mole fraction of  $H_2$ , and  $X_O$  is the mole fraction of O in the mixture.

Of the terms in equation (6),  $\Delta[O]$ ,  $[O]$ , and  $\Delta t$  were measured directly by techniques described in an earlier section Calculation of Rate Constants; however, the concentration of hydrogen  $[H_2]$  and the term in brackets must also be known in order to calculate  $k_2$ . Consider first the term in brackets. Inspection of the equation shows that, for small concentrations of  $H_2$  relative to O, the term in brackets assumes the constant value of 2. This was the case in the investigation of the  $H_2 + O$  reaction performed by Clyne and Thrush (ref. 4).

Unfortunately, in the work presented herein, the concentration of  $H_2$  is high enough so that this simplification cannot be made. The rate constants  $k_3$  and  $k_4$ , however, may be obtained from reference 8, and the term in brackets which will be called  $f$ , can be calculated for experimental conditions of this investigation. It was useful to calculate the rate constant factor  $f$  as a function of temperature at constant initial mole fraction of  $H_2$ , defined as the ratio of the flow rate of hydrogen to the total flow rate ( $F_{H_2}/F_t$ ). The experimental data in figure 3 are used to find  $\Delta[O]/[O]$ , and hence  $[O]$  at constant  $F_{H_2}/F_t$ . Then,  $X_{H_2}/X_O$  was determined with sufficient accuracy from the flow of  $H_2$  into the reactor and the concentration of O. This approximation is satisfactory since only about 5 percent of the  $H_2$  is consumed in the reaction, as will be discussed in the following paragraph. Figure 4 shows a plot of calculated values of  $f$  against temperature. Three curves are shown for three constant values of the  $H_2$  mole fraction  $F_{H_2}/F_t$ , which cover the range of hydrogen concentrations encountered herein. As expected, the value of  $f$  approaches 2 at low temperatures and low  $H_2$  concentrations. The largest deviation of  $f$  from its limiting value of 2 was about 20 percent at the highest temperature and largest  $H_2$  concentration. For most of the experimental conditions, the

deviation of  $f$  from 2 is less than 10 percent. Corrections to the limiting value of 2, resulting from the relatively high  $[H_2]$  in the work presented herein, are minor in nature.

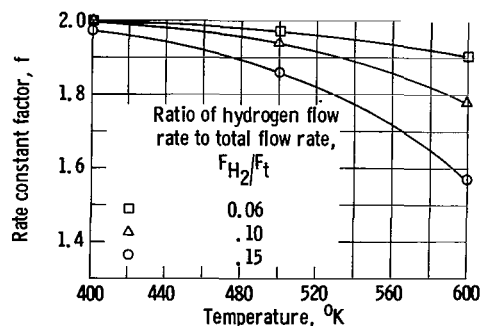


Figure 4. - Calculations of rate constant factor  $f$  for  $H_2 + O \rightarrow OH + H$  reaction.

As mentioned previously, it is also necessary to know the  $[H_2]$  in the reactor in order to calculate  $k_2$ . In principle, the mass spectrometer can be used for this purpose, since it is easily calibrated for  $H_2$ . A large excess of  $H_2$  was used, however, which meant that only a small percentage of the  $H_2$  admitted to the stirred reactor was destroyed

by chemical reaction. Detection of these small changes by the mass spectrometer was possible, but the results were not very useful because of the low precision of the measurements. The amount of  $H_2$  lost, being very small, was calculated with sufficient accuracy from the measured O loss, as described in the following paragraph.

By assuming the steady state for OH, reactions (2), (3), and (4) give for the stirred reactor

$$\frac{\Delta[H_2]}{\Delta t} = -k_2[H_2][O] \left[ 1 + \frac{k_4[H_2]}{k_3[O] + k_4[H_2]} \right] \quad (7)$$

When the ratio of  $H_2$  to O is sufficiently small, as in reference 4, the term in brackets reduces to unity. Dividing equation (5) by equation (7) yields an expression for the relative stoichiometry:

$$\frac{\Delta[O]}{\Delta[H_2]} = \frac{2 + \frac{k_4 X_{H_2}}{k_3 X_O}}{1 + \frac{k_4 X_{H_2}}{k_3 X_O}} \quad (8)$$

This equation shows that the relative number of moles of O reacted per mole of  $H_2$  reacted varies from 2 for small values of the  $H_2$  to O ratio to 0.5 for very large excesses of  $H_2$ .

In practice, it was useful to construct charts of relative stoichiometry as a function of temperature at constant hydrogen flow into the reactor. These were made by interpolating experimental values of  $\Delta[O]/[O]$  at constant values of initial  $H_2$  mole fraction (expressed as a fraction of total flow) from figure 3. These values of  $\Delta[O]/[O]$  were used with experimental values of initial oxygen atom concentration ( $[O]_0$ ) from table I to find  $[O]$ . The  $H_2$  flow into the reactor can be used to calculate the initial molecular hydrogen concentration ( $[H_2]_0$ ), the amount of  $H_2$  that would be present in the absence of chemical reaction. To a sufficiently good approximation,  $[H_2]_0/[O] = X_{H_2}/X_O$ . This fraction can then be used with equation (8) to calculate  $\Delta[O]/\Delta[H_2]$ , the relative stoichiometry. In this way, figure 5(a) was constructed, giving the relative stoichiometry as a function of temperature at constant hydrogen flow expressed as the fraction of the total flow rate,  $F_{H_2}/F_t$ . This figure shows that the relative stoichiometry varies from about 1.1 to 2.0 for the range of experimental variables covered in this report.

The relative stoichiometries derived from figure 5(a) can be used with the experimental values of  $\Delta[O]$  and  $[H_2]_0$  to find  $\Delta[H_2]/[H_2]_0$ , the fraction of  $H_2$  consumed in the reaction. Figure 5(b) shows these fractions as a function of temperature at constant  $H_2$  mole fraction  $F_{H_2}/F_t$ . This figure shows that the amount of  $H_2$  consumed in the reactor is small, ranging from 1 to 10 percent of the  $H_2$  introduced into the reactor. The curves in figure 5(b) can easily be used to calculate  $[H_2]$  in the stirred reactor from experimental values of the  $H_2$  mole fraction  $F_{H_2}/F_t$ .

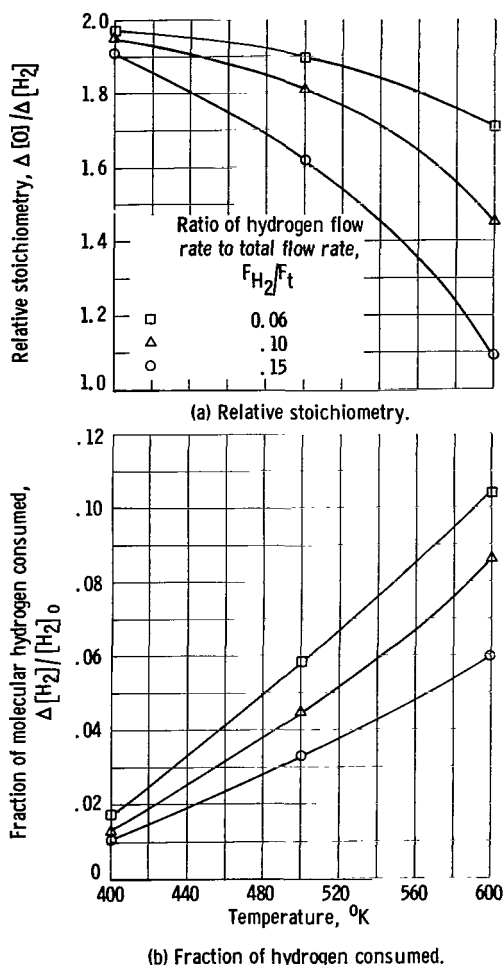


Figure 5. - Calculations of relative stoichiometry and fraction of molecular hydrogen consumed.

tory, considering the completely different methods used and the estimated accuracy of  $\pm 50$  percent for the rate constants of this investigation.

The present authors conclude that the stirred reactor yields rate constants that agree with those obtained by other techniques, within the estimated accuracy of  $\pm 50$  percent.

#### EFFECT OF MOLECULAR OXYGEN ON OXIDATION RATE OF MOLECULAR HYDROGEN BY ATOMIC OXYGEN

In a previous work (ref. 1) the reaction of  $H_2$  with mixtures of  $O_2$  and  $O$  were studied. The overall rate constant defined in equation (1) for the disappearance of  $O$  in the stirred reactor was

$$k_2^O = 2.8 \times 10^{-13} \exp(-8.3/RT) \quad \text{cc}/(\text{mole})(\text{sec}) \quad (9)$$

In summary, the calculation of rate constants  $k_2$  for the reaction  $H_2 + O \rightarrow OH + H$  by using equation (6) requires experimental data for  $\Delta t$ ,  $\Delta[O]$ , and  $[O]$ , all of which were directly measured. In addition, a correction factor  $f$  for water formation is needed, which can be calculated with sufficient accuracy. The remaining experimental data required are for  $[H_2]$  in the reactor. These were determined by application of small calculated correction factors to  $[H_2]_0$  in the reactor in the absence of chemical reaction.

The results of the calculation outlined in the preceding paragraph are given in table I and are shown in figure 6, where a semilogarithmic plot of the rate constant  $k_2$  against reciprocal temperature  $1/T$  is shown. The equation of the line through the data is

$$k_2 = 4.3 \times 10^{-13} \exp(-10.2/RT) \\ \text{cc}/(\text{mole})(\text{sec})$$

This result is compared with data from references 4, 6, and 7 in figure 7. The most recent data covering a range of temperature similar to the range in this report are from reference 4. The rate constants herein average about 20 percent higher than those of reference 4 and the activation energy herein is 0.8 kilocalorie per mole higher than that of reference 4. The agreement is satisfactory.

TABLE I. - STIRRED REACTOR MEASUREMENTS OF ATOMIC OXYGEN WITH MOLECULAR HYDROGEN

Run	Added molecular hydrogen flow (NTP), <sup>a</sup> cc/sec	Temperature, °K	Nitrogen carrier gas flow into discharge (NTP), <sup>a</sup> cc/sec	Nitric oxide gas added or oxygen atoms produced (NTP), <sup>a</sup> cc/sec	Fraction of oxygen atoms consumed in reactor uncorrected for pressure, $\Delta[O]/[O]^*$ (b)	Fraction of oxygen atoms consumed in reactor by reaction with added molecular hydrogen, $\Delta[O]/[O]$	Pressure, mm Hg	Residence time, $\Delta t$ , sec	Fraction of hydrogen gas consumed (calculated), $\Delta[H_2]/[H_2]_0$	Factor relating $k_2$ to $-\Delta[O]/f$ (calculated), <sup>c</sup>	Rate constant, $k_2$ , cc/(mole)(sec)
1a	0.163	396	1.46	0.034	0.15	0.07	0.66	0.13	0.01	2.0	$1.1 \times 10^8$
2a	.314	397	1.46	.033	.24	.12	.69	.13	.01	.01	1.0
3a	.318	397	1.46	.034	.33	.20	.70	.13	.01	2.0	1.6
Average value											$1.2 \times 10^8$
Average deviation											±19 percent
6a	0.200	506	1.46	0.034	1.25	1.17	0.67	0.10	0.04	1.9	$2.4 \times 10^9$
6b	.195	506	↓	.034	.93	.85	.67	↓	.04	1.9	1.9
7b	.195	510	↓	.033	.78	.70	.67	↓	.04	1.9	1.6
8a	.070	510	↓	.034	.40	.37	.64	↓	.07	2.0	2.1
8b	.169	510	↓	.034	.82	.75	.66	↓	.05	1.9	2.0
Average value											$2.0 \times 10^9$
Average deviation											±10 percent
9a	0.060	596	1.46	0.034	1.10	1.07	0.64	0.09	0.12	1.9	$10.7 \times 10^9$
9b	.216	596	↓	.034	3.21	3.12	.68	↓	.08	1.7	10.0
10a	.046	600	↓	.032	.74	.72	.64	↓	.12	2.0	9.3
10b	.093	600	↓	↓	1.31	1.27	.65	↓	.11	1.9	8.3
10c	.200	600	↓	↓	2.24	2.16	.67	↓	.08	1.7	7.4
11a	.038	601	↓	↓	1.48	.46	.64	↓	.12	2.0	6.9
11b	.077	↓	↓	↓	1.01	.98	.64	↓	.11	1.9	7.9
11c	.158	↓	↓	↓	2.47	2.40	.66	↓	.09	1.8	9.9
11d	.250	↓	↓	↓	3.12	3.02	.68	↓	.07	1.6	9.9
Average value											$8.9 \times 10^9$
Average deviation											±13 percent
12a	0.263	399	1.46	0.037	0.19	0.08	0.68	0.13	0.01	2.0	$0.76 \times 10^8$
12b	.254	399	↓	.037	.18	.07	.68	↓	.01	↓	1.2
13a	.107	400	↓	.033	.10	.05	.65	↓	.02	↓	1.2
14a	.138	400	↓	.031	.13	.07	.66	↓	.01	↓	1.2
Average value											$0.96 \times 10^8$
Average deviation											±24 percent
15b	0.213	595	1.44	0.032	2.51	2.42	0.67	0.09	0.08	1.7	$7.7 \times 10^9$
16a	.046	597	↓	.033	.63	.6	.64	↓	.12	2.0	7.5
16b	.132	597	↓	.033	1.62	1.56	.65	↓	.09	1.8	7.6
17a	.020	595	↓	.034	.32	.31	.63	↓	.13	2.0	8.7
17b	.068	↓	↓	↓	.85	.92	.64	↓	.11	1.9	8.3
17c	.269	↓	↓	↓	2.77	2.66	.69	↓	.07	1.5	7.6
17d	.260	↓	↓	↓	2.77	2.66	.68	↓	.07	1.6	7.4
Average value											$7.8 \times 10^9$
Average deviation											±5 percent
18a	0.047	507	1.44	0.032	0.23	0.21	0.64	0.10	0.07	2.0	$1.8 \times 10^9$
18b	.124	↓	↓	↓	.54	.48	.65	↓	.05	2.0	1.6
18c	.213	↓	↓	↓	.91	.82	.67	↓	.04	1.9	1.6
18d	.196	↓	↓	↓	.96	.87	.67	↓	.04	1.9	1.9
19a	.045	509	↓	.031	.22	.20	.64	↓	.07	2.0	1.8
19b	.117	↓	↓	↓	.51	.46	.65	↓	.05	2.0	1.6
19c	.185	↓	↓	↓	.80	.72	.67	↓	.04	1.9	1.6
20a	.030	↓	↓	↓	.15	.13	.63	↓	.08	2.0	1.6
20b	.111	↓	↓	↓	.43	.38	.65	↓	.06	2.0	1.4
20c	.265	↓	↓	↓	1.14	1.03	.69	↓	.03	1.9	1.7
Average value											$1.7 \times 10^9$
Average deviation											±6 percent
21	0.081	451	1.50	0.032	0.08	0.08	0.66	0.11	0.04	2.0	$2.9 \times 10^8$
22	.132	451	↓	↓	.28	.22	.67	.12	.03	2.0	5.2
23	.196	449	↓	↓	.37	.30	.68	↓	.03	2.0	4.8
24	.209	↓	↓	↓	.37	.28	.68	↓	.02	1.9	4.5
25	.210	↓	↓	↓	.45	.36	.69	↓	.02	1.9	5.6
26	.159	↓	↓	↓	.45	.38	.67	↓	.03	2.0	7.4
Average value											$5.1 \times 10^8$
Average deviation											±20 percent
27	0.091	430	1.69	0.035	0.09	0.05	0.70	0.12	0.03	2.0	$1.6 \times 10^8$
28	.078	430	↓	.034	.09	.08	.70	↓	.03	↓	2.3
29	.095	430	↓	.030	.09	.05	.70	↓	.03	↓	1.6
30	.171	425	↓	.027	.30	.22	.67	↓	.02	↓	3.6
31	.184	425	↓	.039	.26	.18	.68	↓	.02	↓	2.7
32	.251	425	↓	.027	.31	.21	.69	↓	.02	↓	2.4
Average value											$2.4 \times 10^8$
Average deviation											±21 percent

<sup>a</sup>Normal temperature and pressure<sup>b</sup> $\Delta[O] = [O]_0$  (initial oxygen atom concentration) -  $[O]$  (final oxygen atom concentration).<sup>c</sup>See p. 8 of text.

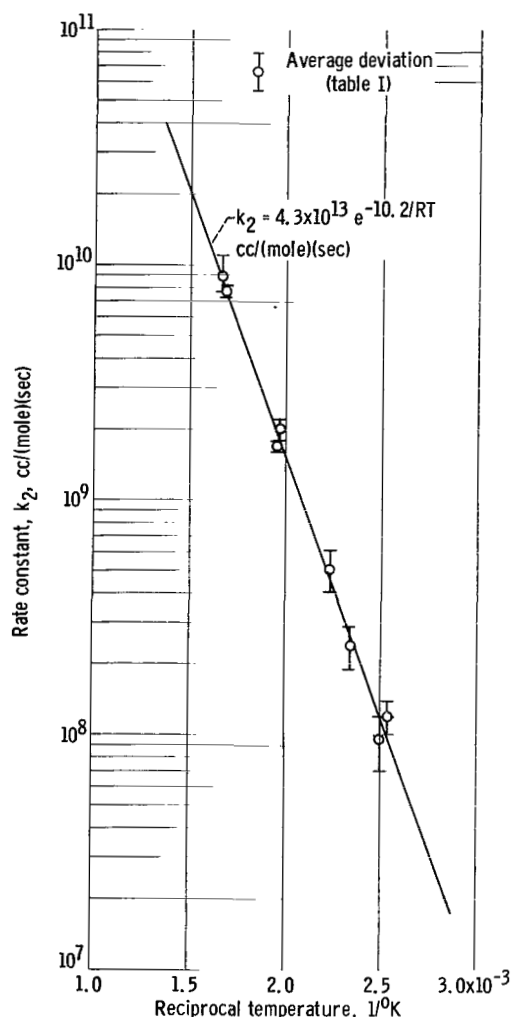


Figure 6. - Rate constants for  $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$  reaction.

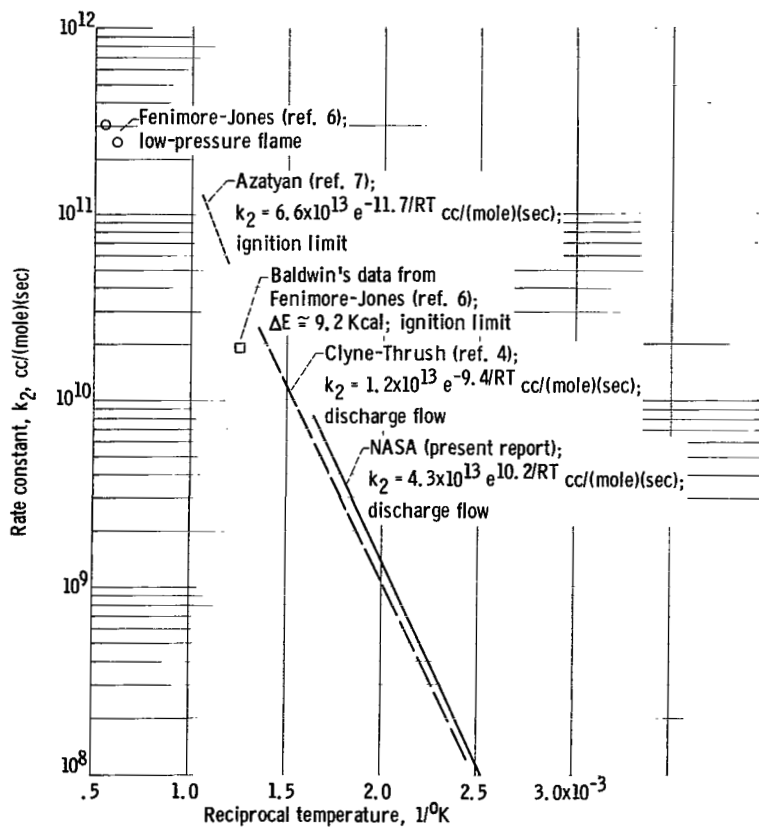


Figure 7. - Comparisons of rate constants for  $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$  reaction.

It is interesting to compare these rate constants with those for the disappearance of O in the absence of  $\text{O}_2$ . In the preceding section, data for the consumption of O were used to calculate rate constants for the reaction  $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$ . These same data (table I) can be used to calculate overall rate constants for oxygen atom disappearance in the absence of  $\text{O}_2$ . Equation (1) defines the overall rate constant  $k$  that is calculated in this way. (Comparison of eqs. (1) and (6) shows that  $k^1 \approx 2k_2$ , since the term in brackets in eq. (6) is approximately 2). The results are shown in figure 8, along with rate constants for an excess of  $\text{O}_2$ . It can be seen that the presence of  $\text{O}_2$  greatly increases the rate of disappearance of O from a factor of 5 at low temperatures to about 3 at high temperatures. In the following paragraphs, this increase in rate is explained.

In the presence of  $\text{O}_2$ , it is necessary to add two reactions to the three-reaction scheme proposed previously for the reaction of  $\text{H}_2$  with O (ref. 4). With these reactions, the reaction scheme for the reaction of  $\text{H}_2$  with  $(\text{O} + \text{O}_2)$  is

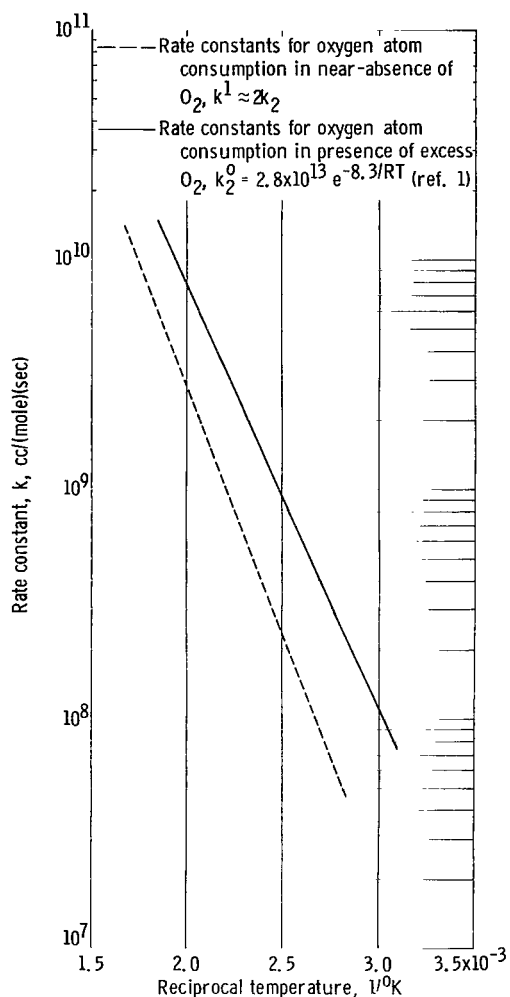
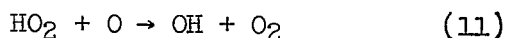
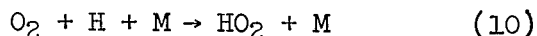
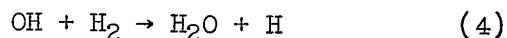


Figure 8. - Comparison of rate constants for oxygen atom consumption for the  $H_2 + O$  reaction.



The purpose herein is to show how the preceding reaction mechanism can explain the effect on the rate of O disappearance produced by  $O_2$ . In order to do this, the reaction mechanism is used with the data for the  $H_2$  with  $O + O_2$  reaction to deduce rate constants for the reaction  $H_2 + O \rightarrow OH + H$ . These rate constants can then be compared with the rate constants obtained in the previous section from the reaction in the absence of  $O_2$ .

On the basis of the preceding reaction mechanism, the oxygen atom decay rate  $-d[O]/dt$  may be expressed as follows:

$$-\frac{d[O]}{dt} = k_2[O][H_2] + k_3[OH][O] + k_{11}[HO_2][O] \quad (12)$$

Then by assuming steady state for hydroxyl radical (OH) and hydroperoxo radical ( $HO_2$ ), equation (12) may be rewritten as

$$-\frac{d[O]}{dt} = k_2[O][H_2] + k_3[OH][O] + k_{10}[H][O_2][M] \quad (13)$$

Expressions for the concentration of atomic hydrogen [H] and [OH] were obtained as follows: For [H] one makes use of the equation

$$\frac{d[H]}{dt} = 2k_2[H_2][O] \quad (14)$$

This equation can be put into the finite-difference form appropriate to the stirred reactor. Since  $[H]_0$  is zero, equation (14) gives

$$[H] = 2k_2[H_2][O]\Delta t \quad (15)$$

where  $\Delta t$  is the residence time in the stirred reactor. For [OH] one finds that

$$[\text{OH}] = \frac{k_2[\text{H}_2][\text{O}](1 + 2k_{10}[\text{O}_2][\text{M}]\Delta t)}{k_3[\text{O}] + k_4[\text{H}_2]} \quad (16)$$

Now after proper substitution and conversion to the finite-difference form, equation (13) may be written as

$$\frac{\Delta[\text{O}]}{\Delta t} = -k_2[\text{H}_2][\text{O}] \left[ \frac{\left( 2 + \frac{k_4 X_{\text{H}_2}}{k_3 X_{\text{O}}} \right) (1 + 2k_{10}[\text{O}_2][\text{M}]\Delta t)}{1 + \frac{k_4 X_{\text{H}_2}}{k_3 X_{\text{O}}}} \right] \quad (17)$$

Values of  $k_2$  were calculated from this equation by using the experimental data for the  $\text{H}_2$  with  $\text{O} + \text{O}_2$  reaction from reference 1 and a value of  $k_{10}$  based on references 9 and 10. Reference 9 reported a value of  $k_{10}$  of  $0.78 \times 10^{16}$  cubic centimeters squared per mole squared per second at  $293^\circ \text{K}$  for  $\text{M} = \text{argon}$  and an activation energy  $\Delta E$  of -1600 calories. Reference 10 provided information to calculate  $k_{10}$  for the experimental conditions of reference 1, where  $\text{M} = \text{O}_2$ . Values of  $k_3$  and  $k_4$  were again taken from reference 8. The results of this calculation are shown in figure 9, where the calculated rate constants are compared with values obtained in near-absence of  $\text{O}_2$  from the preceding section. This figure shows that the calculated rate constants agree fairly well with the values measured more directly. This agreement gives evidence favoring the reaction mechanism proposed for the reaction of  $\text{H}_2$  with  $\text{O} + \text{O}_2$  mixtures. Thus, the increased rate of oxygen atom disappearance in the presence of  $\text{O}_2$  is due to the reaction  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ . The  $\text{HO}_2$  formed in this reaction reacts with  $\text{O}$  to form  $\text{OH}$  and  $\text{O}_2$ . The  $\text{OH}$  formed removes an oxygen atom by reaction to form  $\text{O}_2$  and  $\text{H}$ , thus regenerating  $\text{H}$ . The net effect is that each molecule of  $\text{HO}_2$  that was formed removes two oxygen atoms.

#### REACTION OF AMMONIA WITH ATOMIC OXYGEN

The reaction of  $\text{O}$  and  $\text{NH}_3$  has been studied previously (refs. 1, 5, 11, 12, and 13), but never very thoroughly, and never in the absence of  $\text{O}_2$ . In the present report, the authors have studied the reaction without  $\text{O}_2$ , have measured approximately the stoichiometry for all principal products and reactants, and have suggested a reaction mechanism.

#### Atomic Oxygen Consumption in Stirred Reactor and Order of Reaction

For study of the  $\text{NH}_3 + \text{O}$  reaction,  $\text{O}$  was produced both by the  $\text{N} + \text{NO}$  titration technique and by subjecting a 1.8-percent  $\text{O}_2$ -Ar mixture to a microwave discharge. Since  $\text{NH}_3$  produced a strong peak in the mass spectrometer at  $m/e = 16$ , it was necessary to monitor  $\text{O}$  consumption at  $m/e = 8$  with an ionizing voltage of 85 volts.

This technique was used to measure the amount of  $\text{O}$  consumed in the stirred



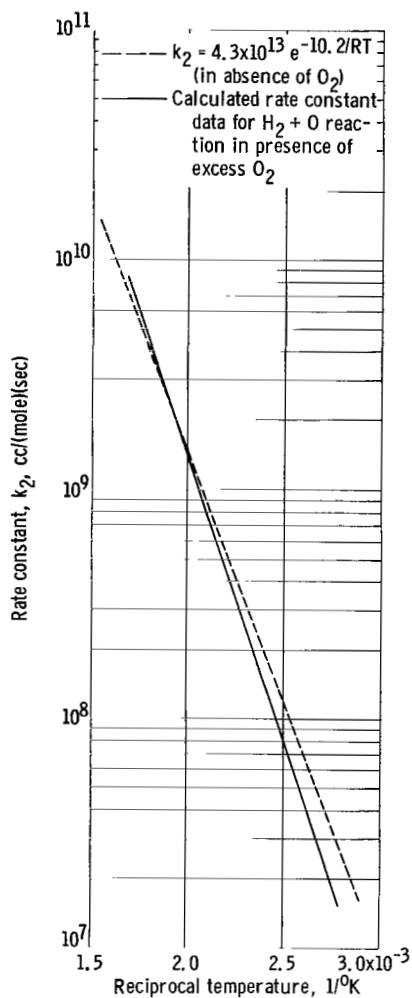


Figure 9. - Calculated rate constants for  $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$  reaction in presence of excess molecular oxygen.

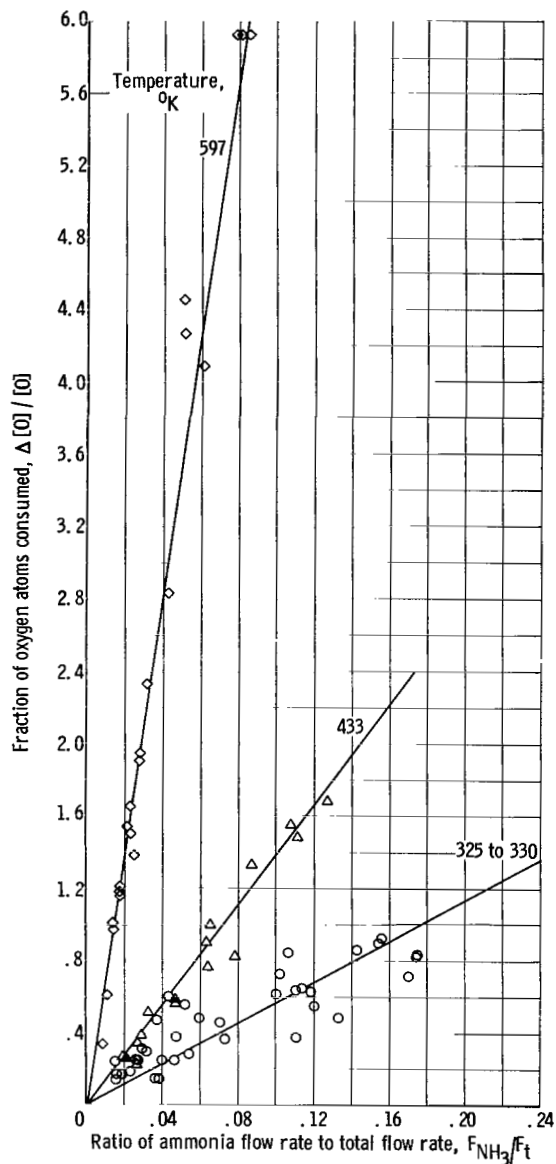


Figure 10. - Oxygen atoms consumed by added ammonia.

reactor at increasing levels of  $\text{NH}_3$  concentration for three temperatures. These data are shown in table II. As discussed previously for  $\text{H}_2$ , the plots of  $\Delta[\text{O}]/[\text{O}]$  against  $F_{\text{NH}_3}/F_t$ , the ratio of the ammonia flow to the total flow, are expected to approximate straight lines for a bimolecular reaction. These plots are shown in figure 10, where  $\Delta[\text{O}]/[\text{O}]$  is indeed directly proportional to  $F_{\text{NH}_3}/F_t$  for all three temperatures. Thus, the reaction is bimolecular and first order in both  $\text{NH}_3$  and  $\text{O}$ , within experimental error.

TABLE II. - STIRRED REACTOR MEASUREMENTS OF ATOMIC OXYGEN WITH AMMONIA  
(a) Atomic nitrogen and nitric oxide technique used as atomic oxygen source

Run	Added ammonia flow (NTP), <sup>a</sup> cc/sec	Temperature, °K	Nitrogen carrier gas flow into discharge (NTP), <sup>a</sup> cc/sec	Nitric oxide gas added or oxygen atoms produced (NTP), <sup>a</sup> cc/sec	Fraction of oxygen atoms consumed in reactor uncorrected for pressure, $\Delta[O]/[O]^*$ (b)	Fraction of oxygen atoms consumed in reactor by reaction with added ammonia, $\Delta[O]/[O]$	Pressure, mm Hg	Residence time, $\Delta t$ , sec	Relative stoichiometry, $\Delta[O]/\Delta[NH_3]$ or $\Delta[O]/\Delta[NO]$	Rate constant for oxygen atom consumption, $k_{22}$ , cc/(mole)(sec)
1a	0.077	320	1.55	0.020	0.42	0.38	0.67	0.15	4.4	$1.6 \times 10^9$
2a	.051	323	↓	.034	.32	.30	.66	↓	↓	2.0
2b	.193	323	↓	.034	.71	.64	.69	↓	↓	1.1
3a	.043	325	↓	.037	.27	.25	.66	↓	↓	2.0
3b	.200	325	↓	.037	.73	.65	.69	↓	↓	1.1
4a	.042	330	↓	.020	.27	.25	.66	↓	↓	2.1
Average value Average deviation										$1.7 \times 10^9$ ±22 percent
5a	0.057	328	1.51	0.030	0.18	0.15	0.66	0.16	4.4	$0.85 \times 10^9$
6a	.059	328	↓	.036	.18	.15	.66	↓	↓	.81
6b	.236	331	↓	↓	.59	.49	.69	↓	↓	.72
7a	.035	330	↓	↓	.21	.19	.66	↓	↓	1.8
7b	.323	↓	↓	↓	.96	.83	.71	↓	↓	.89
7c	.253	↓	↓	↓	.96	.86	.69	↓	↓	1.2
8b	.170	↓	↓	↓	.69	.62	.68	↓	↓	1.2
9a	.096	↓	↓	.033	.52	.48	.66	↓	↓	1.7
9b	.283	↓	↓	.033	1.04	.93	.70	↓	↓	1.1
10a	.087	↓	↓	.029	.32	.28	.66	↓	↓	1.1
10b	.203	↓	↓	.029	.71	.63	.68	↓	↓	1.1
Average value Average deviation										$1.1 \times 10^9$ ±22 percent
11a	0.221	443	1.51	0.035	1.77	1.68	0.69	0.12	4.4	$4.6 \times 10^9$
12a	.042	440	↓	.035	.36	.34	.67	↓	↓	4.7
12b	.104	440	↓	.035	.82	.77	.66	↓	↓	4.4
13a	.074	433	↓	.034	.62	.58	.66	↓	↓	4.5
14a	.046	432	↓	.027	.41	.39	.66	↓	↓	4.8
14b	.129	433	↓	↓	.88	.82	.67	↓	↓	3.6
15a	.033	↓	↓	↓	.28	.26	.67	↓	↓	4.4
15b	.106	↓	↓	↓	1.05	1.00	.66	↓	↓	5.4
15c	.181	↓	↓	↓	1.63	1.55	.68	↓	↓	4.9
16a	.034	↓	↓	.024	.28	.26	.67	↓	↓	4.2
16b	.052	↓	↓	↓	.54	.51	.66	↓	↓	5.6
16c	.102	↓	↓	↓	.95	.90	.66	↓	↓	5.1
16d	.190	↓	↓	↓	1.56	1.48	.68	↓	↓	4.5
17a	.040	432	↓	.027	.24	.22	.65	↓	↓	3.0
17b	.072	432	↓	.027	.61	.58	.66	↓	↓	4.5
17c	.146	432	↓	.027	1.39	1.33	.67	↓	↓	5.2
Average value Average deviation										$4.6 \times 10^9$ ±10 percent
18a	0.028	593	1.51	0.036	1.21	1.20	0.65	0.087	4.4	$5.3 \times 10^{10}$
18b	.069	594	↓	↓	2.86	2.83	.66	↓	↓	4.7
18c	.140	593	↓	↓	5.94	5.88	.67	↓	↓	4.7
18d	.135	593	↓	↓	5.94	5.88	.67	↓	↓	4.9
19a	.044	596	↓	.032	1.97	1.95	.66	↓	↓	5.2
19b	.083	596	↓	.032	4.27	4.23	.66	↓	↓	5.9
19c	.130	596	↓	↓	5.99	5.93	.67	↓	↓	5.1
20a	.036	597	↓	↓	1.52	1.50	.66	↓	↓	5.1
20b	.083	↓	↓	↓	4.50	4.46	.66	↓	↓	6.2
20c	.143	↓	↓	↓	8.57	8.51	.67	↓	↓	6.7
21a	.023	↓	↓	.029	.99	.98	.65	↓	↓	5.1
21b	.044	↓	↓	↓	1.94	1.92	.65	↓	↓	5.0
22a	.050	↓	↓	↓	2.36	2.34	.65	↓	↓	5.5
22b	.097	↓	↓	↓	4.13	4.09	.66	↓	↓	4.7
Average value Average deviation										$5.3 \times 10^{10}$ ±8 percent

<sup>a</sup>Normal temperature and pressure.

<sup>b</sup> $\Delta[O] = [O]_0$  (initial oxygen atom concentration) -  $[O]$  (final oxygen atom concentration).

TABLE II. - Continued. STIRRED REACTOR MEASUREMENTS OF ATOMIC OXYGEN WITH AMMONIA  
(a) Concluded. Atomic nitrogen and nitric oxide technique used as atomic oxygen source

Run	Added ammonia flow (NTP), <sup>a</sup> cc/sec	Temperature, °K	Nitrogen carrier gas flow into discharge (NTP), <sup>a</sup> cc/sec	Nitric oxide gas added or oxygen atoms produced (NTP), <sup>a</sup> cc/sec	Fraction of oxygen atoms consumed in reactor uncorrected for pressure, $\Delta[O]/[O]^*$ (b)	Fraction of oxygen atoms consumed in reactor by reaction with added ammonia, $\Delta[O]/[O]$	Pressure, mm Hg	Residence time, $\Delta t$ , sec	Relative stoichiometry, $\Delta[O]/\Delta[NH_3]$ or $\Delta[O]/\Delta[NO]$	Rate constant for oxygen atom consumption, $k^{22}$ , cc/(mole)(sec)
23b	0.182	324	1.51	0.030	0.93	0.85	0.68	0.16	4.4	$1.5 \times 10^9$
23c	.175	324		.030	.80	.73	.68			1.3
24b	.083	326		.033	.60	.56	.66			2.2
25a	.025	326		.029	.16	.15	.65			1.9
26a	.024	326		.033	.17	.16	.65			2.3
26b	.116	331		.033	.51	.46	.67			1.3
26d	.279			.033	1.01	.90	.70			1.1
27a	.029			.036	.18	.17	.65			1.9
27b	.120			.036	.42	.37	.67			1.0
28a	.063			.028	.28	.25	.65			1.3
28b	.207			.028	.64	.55	.69			.9
28a	.073			.029	.27	.24	.65			1.1
Average value Average deviation										$1.5 \times 10^8$ ±27 percent
30a	0.015	588	1.51	0.030	0.35	0.34	0.65	0.088	4.4	$2.7 \times 10^{10}$
31	.021	593		.029	1.01	1.00		.087		5.9
32	.026	594		.024	1.21	1.19		.087		5.3
33	.038	591		.020	1.40	1.38		.087		3.9
34	.029	589		.026	1.20	1.19		.088		4.6
35	.017	589		.022	.61	.60	.64	.088		4.1
36	.034	595		.022	1.65	1.63	.65	.087		5.5
37	.033	595		.022	1.55	1.53	.65	.087		5.3
Average value Average deviation										$4.7 \times 10^{10}$ ±18 percent

<sup>a</sup>Normal temperature and pressure.

<sup>b</sup> $\Delta[O] = [O]_0$  (initial oxygen atom concentration) -  $[O]$  (final oxygen atom concentration).

### Products of Reaction

In reference 1, the principal products of the  $NH_3$  with  $O_2 + O$  reaction were NO and  $H_2O$ ; the secondary product was  $H_2$ , with possibly a trace of H.

In the work reported herein, the products were measured from  $NH_3$  reacting with O produced from the N + NO reaction. As before, the principal products included NO and  $H_2O$ ; however, a mass spectrometer peak at  $m/e = 32$  was also observed. This could not have been detected in reference 1 because of the excess of  $O_2$  present. The peak at  $m/e = 32$  could arise either from  $O_2$  or from hydrazine ( $N_2H_4$ ). In order to differentiate between the two, fully deuterated ammonia  $ND_3$  was reacted with O free of  $O_2$ . The peak at  $m/e = 32$  did not shift, so that it must have originated from  $O_2$ , and not from  $N_2H_4$ .

When O from the N + NO reaction is used, a large excess of  $N_2$  is present, so that any  $N_2$  formed as a reaction product could escape undetected. To test this possibility,  $NH_3$  was reacted with O produced by a microwave discharge through a dilute 1.8-percent  $O_2$ -Ar mixture. No  $N_2$  could be detected.

In the experiments described in table II,  $H_2$  was detectable as a minor product although H was not. There was no nitrogen-containing product other than NO;  $O_2$ ,  $H_2$ , and  $H_2O$  were the remaining reaction products.

### Stoichiometry of Reaction

Since there is no nitrogen-containing product other than NO, each mole of

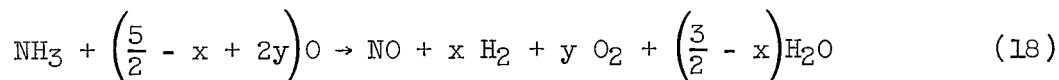
TABLE II. - Concluded. STIRRED REACTOR MEASUREMENTS OF ATOMIC OXYGEN WITH AMMONIA

(b) 1.8 Percent molecular oxygen - argon mixture used as atomic oxygen source

Run	Added ammonia flow (NTP), <sup>a</sup> cc/sec	Temperature, °K	Oxygen carrier gas flow into discharge (NTP), <sup>a</sup> cc/sec	Fraction of oxygen atoms consumed in reactor uncorrected for pressure, $\Delta[O]/[O]^*$	Fraction of oxygen atoms consumed in reactor by reaction with added ammonia, $\Delta[O]/[O]$	Initial oxygen atom or nitrogen dioxide concentration, $[O]_0$ cc/sec (b)	Pressure, mm Hg	Residence time, $\Delta t$ , sec	Relative stoichiometry, $\Delta[O]/\Delta[NH_3]$ or $\Delta[O]/\Delta[NO]$	Rate constant for oxygen atom consumption, $k_{22}^{(O)}$ cc/(mole)(sec)
1a	0.103	306	1.50	0.31	0.26	(0.04)	0.65	0.17	4.4	$7.1 \times 10^8$
1b	.097			.46	.42					13.0
1c	.097			.35	.31					9.2
3a	.042			.24	.22		.64			14.7
3b	.039			.26	.24		.64			17.9
Average value										$1.2 \times 10^9$
Average deviation										±29 percent
4a	0.0087	541	1.50	0.34	0.34	(0.04)	0.64	0.10	4.4	$4.4 \times 10^{10}$
4b	.0072	553		.35	.35			.09		6.3
4c	.0077	559		.38	.38					6.5
4d	.0064	561		.37	.37					8.5
5a	.032	566		1.95	1.93					6.9
5b	.035	567		1.76	1.74					5.7
5c	.058	567		3.06	3.08		.65			5.6
Average value										$6.3 \times 10^{10}$
Average deviation										±14 percent
1'a	0.0092	565	1.50	0.42	0.42	(0.04)	0.64	0.09	4.4	$5.9 \times 10^{10}$
1'b	.0092			.58	.58					9.1
1'c	.0083			.44	.44					7.3
1'd	.0083			.60	.60					11.3
2'b	.033			1.96	1.94		.65			6.6
3a	.081			5.64	5.60		.65			7.7
3b	.081			5.92	5.88		.65			8.1
Average value										$8.0 \times 10^{10}$
Average deviation										±16 percent
5'a	0.036	428	1.50	0.58	0.56	(0.04)	0.67	0.12	4.4	$9.0 \times 10^9$
5'b	.041			.52	.50					6.9
5'c	.036			.52	.50					7.9
6'a	.133			1.66	1.60		.66			10.9
6'b	.131			1.59	1.53		.66			6.7
7'a	.252			2.85	2.74		.69			6.3
7'b	.232			2.69	2.59		.68			6.5
8'a	.104			1.17	1.12		.66			6.0
8'b	.102			1.28	1.23		.66			6.7
9'a	.194			2.29	2.20		.65			6.4
9'b	.196			2.34	2.25		.66			6.4
Average value										$7.2 \times 10^9$
Average deviation										±15 percent
10'a	0.057	305	1.50	0.34	0.31	(0.04)	0.65	0.17	4.4	$1.5 \times 10^9$
10'b	.057	307		.35	.32		.65			1.6
11'a	.149	306		.68	.61		.67			1.2
11'b	.148	306		.68	.61		.67			1.2
12'b	.276	306		1.12	1.01		.70			1.1
14'a	.062	305		.31	.28		.65			1.3
14'b	.062			.25	.22					1.0
14'c	.065			.32	.29					1.3
14'd	.062			.30	.27					1.3
15'a	.128			.51	.45			.16		1.0
15'b	.125			.58	.52		.66	.17		1.0
16'a	.273			.97	.86		.70			.9
16'b	.252			.97	.86		.69			1.0
Average value										$1.2 \times 10^9$
Average deviation										±17 percent

<sup>a</sup>Normal temperature and pressure.<sup>b</sup>Estimated initial oxygen atom concentration  $[O]_0$  based on approximately 75 percent molecular oxygen dissociation.

$NH_3$  used in the reaction must yield one mole of  $NO$ . If arbitrary values of  $x$  and  $y$  are assigned to the moles of hydrogen and oxygen produced in the reaction, the reaction can be written as



Study of this equation shows that  $x$  is limited in value to  $0 \leq x \leq 3/2$ ,

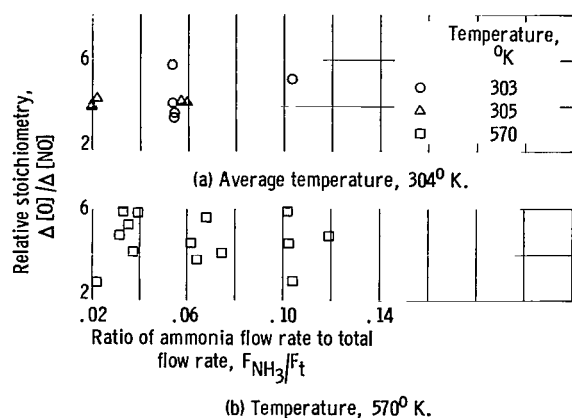


Figure 11. - Measured relative stoichiometry for ammonia - atomic oxygen reaction; source of oxygen atoms, dilute molecular oxygen - argon mixture.

with much greater accuracy than  $\Delta[NH_3]$ , since the initial concentration of NO is zero. Values of  $\Delta[O]/\Delta[NO]$  are shown in figure 11. Much experimental scatter is seen in the data, especially at high temperatures. The average value of  $\Delta[O]/\Delta[NO]$ , neglecting any possible trend with temperature, is 4.4.

Further proof for the previous relative stoichiometry value of 4.4 was obtained by some measurements of  $\Delta[O]/\Delta[NH_3]$  that were made at temperatures of 325° and 580° K. Only the higher temperature results were reliable because, at the lower temperatures, values of  $\Delta[NH_3]$  were too small to measure. At 580° K, the value of  $\Delta[O]/\Delta[NH_3]$  was 4 to 5 agreeing with the previously established  $\Delta[O]/\Delta[NO]$  value of 4.4.

In order to determine the other stoichiometric ratios,  $\Delta[O]/\Delta[O_2]$  and  $\Delta[O]/\Delta[H_2]$ , the values of  $\Delta[O]_f$ ,  $\Delta[O_2]_f$ , and  $\Delta[H_2]_f$ , the changes in flow rates of these species, were measured as a function of  $NH_3$  flow rate. These results are shown in figure 12. Values for the stoichiometric ratios were obtained by drawing mean lines through the data and dividing the slopes of the  $\Delta[O]_f$  line by the slope of the  $\Delta[O_2]_f$  or  $\Delta[H_2]_f$  lines, as shown in the table on page 20. No significant trends with temperature were noted. The average value for  $\Delta[O]/\Delta[O_2]$  was 3.7 and for  $\Delta[O]/\Delta[H_2]$  was 9.

Additional stoichiometric information was obtained by measuring  $\Delta[H_2O]$ . Here it was convenient to measure  $[H_2O]$  in terms of ion currents because of the difficulty of calibrating for  $H_2O$ . These results are compared with ion currents for  $\Delta O_2$  and  $\Delta H_2$  in figure 13. This figure shows that  $\Delta[H_2O]$  lies about midway between  $\Delta[O]$  and  $\Delta[H_2]$ . Since  $\Delta[O]/\Delta[O_2]$  is approximately 3.7 and  $\Delta[O]/\Delta[H_2]$  is approximately 9,  $\Delta[O]/\Delta[H_2O]$  must be about 6.

The two more reliable stoichiometric ratios  $\Delta[O]/\Delta[NO]$  and  $\Delta[O]/\Delta[O_2]$  can be used to calculate the reaction stoichiometry. Equation (18) shows that

but  $y$  can vary from zero to positive infinity. Also, since there are only two unknowns,  $x$  and  $y$ , the complete stoichiometry of the reaction can be obtained from measurement of only two components, such as  $O$  and  $O_2$ , relative to  $NO$  or  $NH_3$ .

In order to determine one of the necessary coefficients, measurements of the atomic oxygen stoichiometry  $\Delta[O]/\Delta[NH_3]$  were made. This was done by measuring the ratio  $\Delta[O]/\Delta[NO]$  since it was found that each mole of  $NH_3$  consumed yields one mole of  $NO$ . Measurements of  $\Delta[O]/\Delta[NO]$  are preferred to those of  $\Delta[O]/\Delta[NH_3]$  because the value of  $\Delta[NO]$  can be measured

Temperature, °K	$\Delta[\text{O}]/\Delta[\text{O}_2]$	$\Delta[\text{O}]/\Delta[\text{H}_2]$	$\Delta[\text{O}]/\Delta[\text{H}_2\text{O}]$	$\Delta[\text{O}]/\Delta[\text{NO}]$
325	3	9 to 10	6 to 7	-----
437	3	9	4 to 5	-----
569	5	9	5 to 9	-----
Average	3.7	9	~6	4.4 (fig. 11)

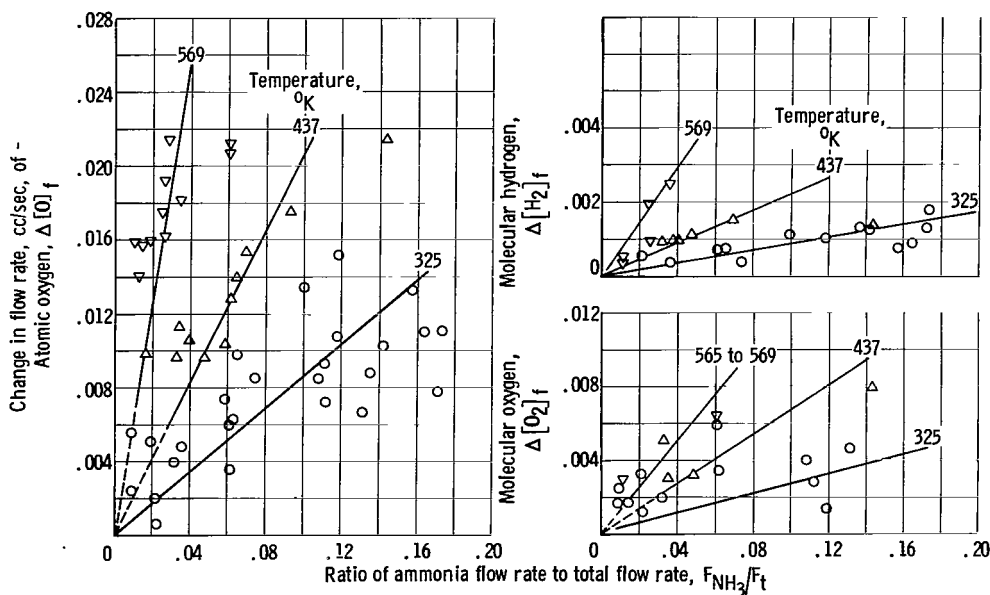


Figure 12. - Changes in flow rates of atomic oxygen, molecular oxygen, and molecular hydrogen for ammonia - atomic oxygen reaction at conditions of normal temperature and pressure.

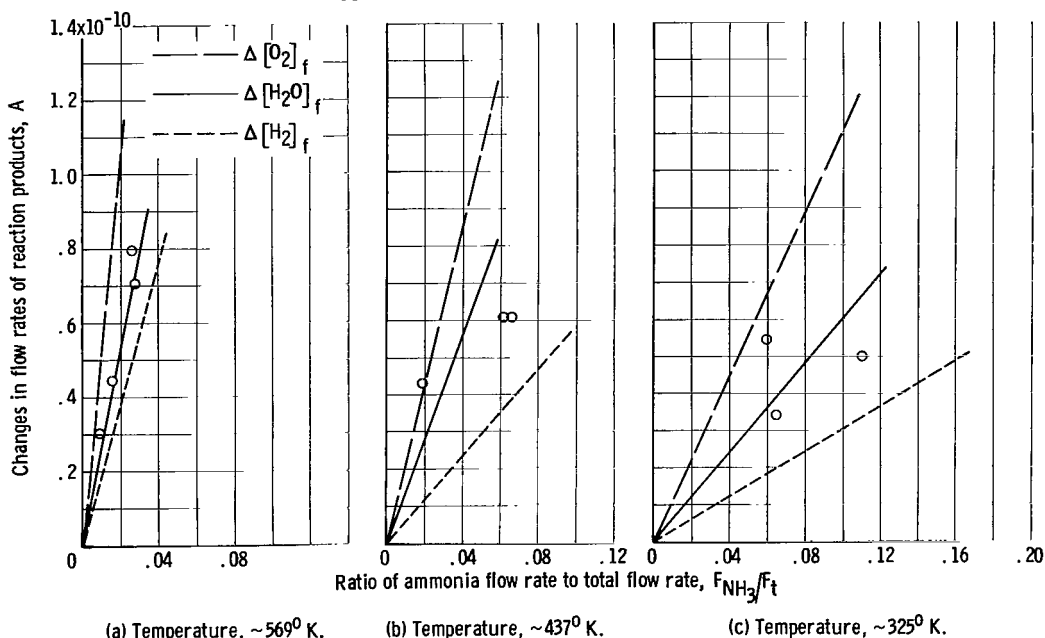


Figure 13. - Changes in flow rates of molecular oxygen, molecular hydrogen, and water for ammonia - atomic oxygen reaction in terms of ion current.

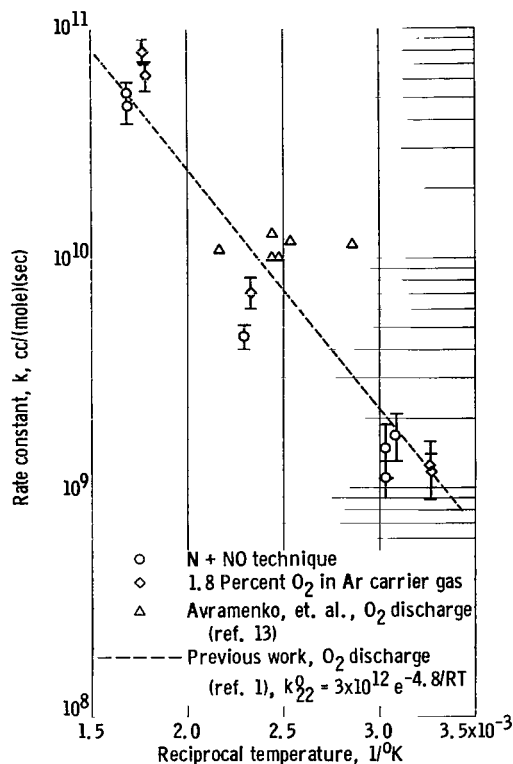


Figure 14. - Rate constants for oxygen atom consumption due to added ammonia.

$$\frac{\Delta[\text{O}]}{\Delta[\text{NO}]} = \frac{5}{2} - x + 2y$$

$$\approx 4.4$$

(19)

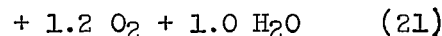
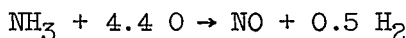
and

$$\frac{\Delta[\text{O}]}{\Delta[\text{O}_2]} = \frac{5}{2y} - \frac{x}{y} + 2$$

$$\approx 3.7$$

(20)

From the experimental values of these ratios it was found that  $x$  is approximately 0.5 and  $y$  is approximately 1.2. The reaction can then be written as



The ratio  $\Delta[\text{O}]/\Delta[\text{H}_2]$  derived from equation (21) is 9, which is in good agreement with the value of 9 obtained experimentally. Similarly, the ratio  $\Delta[\text{O}]/\Delta[\text{H}_2\text{O}]$  from equation (21) is 4, which agrees qualitatively with the experimental value of 6.

#### Rate Constants for Consumption of Atomic Oxygen

The data on O consumption were used with equation (1) to calculate bimolecular rate constants. The  $\text{NH}_3$  concentration required for this was calculated from the  $\text{NH}_3$  flow into the reactor by subtracting from it the  $\text{NH}_3$  consumed. The amount of  $\text{NH}_3$  consumed was calculated from the amount of O consumed and the reaction stoichiometry. The results are plotted in figure 14. Data for O produced both from N + NO and from  $\text{O}_2$  + Ar are shown and compared with data from reference 1 for O +  $\text{O}_2$  mixtures, shown as a dashed line, and Avramenko's work (ref. 13).

It is interesting to note in figure 14 that the rate constant is unaffected by the presence or absence of excess  $\text{O}_2$  within experimental error. This is quite different from the oxidation of hydrogen where the rate constant was increased about a factor of 4 by excess  $\text{O}_2$ . It follows that  $\text{O}_2$  does not play a significant role in the oxidation of  $\text{NH}_3$ . The rate constant for O consumption  $k_{22}^0$  can be taken to be  $3 \times 10^{12} \exp(-4.8/RT)$  cubic centimeter per mole per second as found in reference 1.

### A Possible Reaction Mechanism

A series of reaction steps can be written to account for the reaction products. The most plausible set of reactions is as follows:



Other reactions certainly occur but are thought to be of minor importance.

The initial reaction step must be the attack of  $\text{NH}_3$  by  $\text{O}$ . By analogy with  $\text{H}_2$ , the products are thought to be the amino radical ( $\text{NH}_2$ ) and  $\text{OH}$ . The amino radical is expected to be very reactive, and a reaction with  $\text{O}$  probably predominates. By analogy with the initial step, the products are probably the imino radical ( $\text{NH}$ ) and  $\text{OH}$ . The imino radical can react with  $\text{O}$  to give  $\text{NO}$  and  $\text{H}$ . This reaction is energetically possible and is the most plausible process that yields  $\text{NO}$ . The appearance of  $\text{O}_2$  among the products can be accounted for by the reaction of  $\text{OH}$  and  $\text{O}$ , which is known to be extremely fast. The reaction of  $\text{OH}$  and  $\text{NH}_3$  to yield  $\text{NH}_2$  and  $\text{H}_2\text{O}$  is the most plausible reaction for the production of  $\text{H}_2\text{O}$ . The appearance of  $\text{H}_2$  and the absence of hydrogen atoms among the products can be accounted for by the  $\text{NO}$  catalyzed hydrogen atom recombination reactions shown in equations (27) and (28). Reaction (27) was selected over alternate reactions since it is known to be fast (ref. 14).

The preceding reaction mechanism can also explain why the rate constant is unaffected by the presence or absence of excess  $\text{O}_2$ , since the termolecular reaction  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$  is relatively unimportant because reaction (27) is so fast.

The reaction mechanism outlined in equations (22) to (28) can be used to relate the  $\text{O}$  consumption rate constant  $k_{22}^0$  to the rate constant  $k_{22}$  for the initial oxidation step  $\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH}$ . With the steady state assumed for  $\text{NH}_2$ ,  $\text{NH}$ , and  $\text{OH}$ , it can be shown that

$$k_{22} = \frac{\Delta[\text{O}] - \Delta[\text{O}_2] - 2\Delta[\text{NO}]}{\Delta t [\text{O}][\text{NH}_3]} \quad (29)$$

where the differentials have been replaced by finite differences appropriate to the stirred reactor. Defining  $A$  as



$$A = \frac{\Delta[O] - \Delta[O_2] - 2\Delta[NO]}{\Delta[O]} \quad (30)$$

and recalling from equation (1) that

$$k_{22}^O = \frac{\Delta[O]}{\Delta t[O][NH_3]} \quad (31)$$

then

$$k_{22} = Ak_{22}^O. \quad (32)$$

From the experimental stoichiometry,

$$A = \frac{4.4 - 1.2 - 2}{4.4} = 0.27 \quad (33)$$

so that

$$k_{22} = 0.27 k_{22}^O \quad (34)$$

or

$$k_{22} = 1 \times 10^{12} \exp(-4800/RT) \quad \text{cc}/(\text{mole})(\text{sec}) \quad (35)$$

## CONCLUSIONS

The reactions of atomic oxygen with hydrogen and ammonia were studied mass spectrometrically for the temperature range 350° to 600° K. The investigation resulted in the following conclusions:

1. The stirred reactor technique yields rate constants for the  $H_2 + O \rightarrow OH + O$  reaction in satisfactory agreement with results obtained by the use of other techniques.

2. In the oxidation of molecular hydrogen by atomic oxygen, the rate of atomic oxygen consumption is increased by a factor of 3 to 5 by the presence of an excess of molecular oxygen. This can be accounted for quantitatively by the reaction sequence  $H + O_2 + M \rightarrow HO_2 + M$ ;  $HO_2 + O \rightarrow OH + O_2$ ;  $OH + O \rightarrow O_2 + H$ .

3. The rate of the ammonia - atomic-oxygen reaction is unaffected within experimental error by the presence or absence of molecular oxygen, which indicates that molecular oxygen plays no role in this oxidation.

4. The stoichiometry of the ammonia - atomic-oxygen reaction is  $NH_3 + 4.4 O \rightarrow NO + 0.5 H_2 + 1.2 O_2 + 1.0 H_2O$ .

5. A tentative reaction mechanism for the ammonia-atomic oxygen reaction can be constructed consistent with the experimental results.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, November 18, 1964.

#### REFERENCES

1. Wong, Edgar L.; and Potter, A. E., Jr.: Reaction Rates of Hydrogen, Ammonia, and Methane with Mixtures of Atomic and Molecular Oxygen. Jour. Chem. Phys., vol. 39, no. 9, Nov. 1, 1963, pp. 2211-2217.
2. Kistiakowsky, G. B.; and Volpi, G. G.: Reactions of Nitrogen Atoms. I. Oxygen and Oxides of Nitrogen. Jour. Chem. Phys., vol. 27, no. 5, Nov. 1957, pp. 1141-1149.
3. Kaufman, F.: Reactions of Oxygen Atoms. Prog. in Reaction Kinetics, Pergamon Press, 1961, pp. 1-40.
4. Clyne, M. A. A.; and Thrush, B. A.: Rates of Elementary Processes in the Chain Reaction between Hydrogen and Oxygen. I. Reactions of Oxygen Atoms. Proc. Roy. Soc. (London), ser. A, vol. 275, no. 1363, Oct. 1963, pp. 544-558.
5. Harteck, P.; and Kopsch, U.: Gas Reactions with Atomic Oxygen. Zs. Physik. Chem., ser. B, vol. 12, 1931, pp. 327-347.
6. Fenimore, C. P.; and Jones, G. W.: Rate of Reaction,  $O + H_2 \rightarrow OH + H$ , in Flames. Jour. Phys. Chem., vol. 65, no. 6, June 26, 1961, pp. 993-995.
7. Azatyan, V. V.; Voevodsky, V. V.; and Nalbandyan, A. B.: Determination of the Rate Constant of the Reaction of Atomic Oxygen and Molecular Hydrogen. Kinetika i Kataliz, vol. 2, no. 3, May-June 1961, pp. 340-349.
8. Kaufman, F.: Fast Reactions of OH Radicals. Ninth Symposium (International) on Combustion, Reinhold Pub. Corp., 1962, pp. 659-666.
9. Clyne, M. A. A.; and Thrush, B. A.: Rates of Elementary Processes in the Chain Reaction between Hydrogen and Oxygen. II. Kinetics of the Reaction of Hydrogen Atoms with Molecular Oxygen. Proc. Roy. Soc. (London), ser. A, vol. 275, no. 1363, Oct. 1963, pp. 559-574.
10. Lewis, B.; and von Elbe, G.: Combustion, Flames, and Explosions of Gases. Academic Press, Inc., 1951, pp. 33-34.
11. Moore, Gordon E.; Shuler, Kurt E.; Silverman, Shirleigh; and Herman, Robert: The Reactions of Ammonia and Hydrazine with Oxygen Atoms and Hydrogen Atoms in Atomic Flames. Jour. Phys. Chem., vol. 60, no. 6, June 19, 1956, pp. 813-815.

12. Fenimore, C. P.; and Jones, G. W.: Oxidation of Ammonia in Flames. Jour. Phys. Chem., vol. 65, no. 2, Feb. 24, 1961, pp. 298-303.
13. Avramenko, L. I.; Kolesnikova, R. V.; and Kuznetsova, N. L.: Rate Constant for the Reaction Between Oxygen Atoms and Ammonia. Izv. Akad. Nauk., S.S.S.R. Otd. Khim. Nauk., vol. 6, 1962, pp. 983-989.
14. Clyne, M. A. A.: Rates of Some Atomic Reactions Involving Hydrogen, and Oxygen. Ninth Symposium (International) on Combustion, Academic Press, 1963, pp. 211-219.

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